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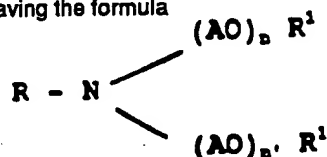
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(54) Concentrated liquid compositions based on N-phosphonomethylglycine

(57) Liquid suspensions in an organic or aqueous organic solvent medium, contain:

a) herbicidal N-phosphonomethylglycine and/or one of its derivatives having an inherent solubility in water of more than 5 g/l, this N-phosphonomethylglycine and/or its derivative being present in the compositions in a proportion of at least 100 g/l glyphosate equivalent, at least part of this N-phosphonomethylglycine or its derivatives being in a form insoluble in the medium under consideration, and

b) a surfactant having an activator character and having the formula



In which

R is a straight-chain or branched alkyl or alkenyl hydrocarbon chain (8 to 22 carbon atoms),  
 A represents an alkylene group,  
 n + n' is between 2 and 40 and preferably between 20 and 25.  
 R<sup>1</sup> is H or acyl.

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CONCENTRATED LIQUID COMPOSITIONS BASED ON  
N-PHOSPHONOMETHYLGLYCINE

The present invention relates to new concentrated formulations based on N-phosphonomethylglycine or compounds containing an N-phosphonomethylglycyl group.

N-Phosphonomethylglycine (sometimes called  
5 glyphosate), and the analogous compounds, their herbicidal properties and the formulations containing them are described in particular in US Patent 3,799,758. Although numerous water-soluble or water-insoluble derivatives of glyphosate are known, in fact  
10 it is very generally preferred to use the water-soluble derivatives and it is for this reason that it is the salts of N-phosphonomethylglycine which have been generally developed or marketed, especially the isopropylammonium salt.

15 More recently (European Patent Application No. 290416) it has been sought to develop concentrates based on N-phosphonomethylglycine salts, which can contain N-phosphonomethylglycine in acid form but in all circumstances contain this N-phosphonomethylglycine  
20 and/or its derivatives in soluble or solubilized forms, these concentrates being solutions characterized by the presence of an activator which is an alkoxyated amine of a particular type. This alkoxyated amine must have at most 12 alkoxy groups per molecule and it must have  
25 a surfactant character and it must promote the herbicidal activity of N-phosphonomethylglycine derivatives. It can be used in a smaller amount than

surfactants in the known formulations of

N-phosphonomethylglycine, at least with regard to the production of concentrates intended for application in the open air, in the form of dilute spraying mixtures, at a rate of 100 to 600 l/ha.

5        Formulations have also been proposed (US Patent 4528023) which contain the tetraaluminium salt of N-phosphonomethylglycine, which is virtually insoluble in water, as well as a surfactant of a special type. One of the consequences of this insolubility of the active  
10 substance is that when the concentrate is diluted in water to obtain the final spraying mixture for spraying, this spraying mixture is not in the form of a perfect solution, which is prejudicial to the application and to obtaining a satisfactory efficacy.  
15 However, those skilled in the art have not attempted to apply the formulations of US-A-4528023 to active substances of higher solubility because experience shows that the production of concentrated suspensions from partially soluble active substances encounters  
20 very great difficulties due to a tendency of the concentrated suspensions to solidify. One of the explanations for these difficulties and this solidification is that there is a pronounced tendency for growth of the crystals in the continuous (aqueous)  
25 phase of the suspensions, this growth being able to develop extremely until solidification occurs.

One aim of the present invention is to provide compositions based on N-phosphonomethylglycine or its

derivatives having an active substance concentration clearly higher than that of similar compositions known in the prior art.

Another aim of the present invention is to provide  
5 compositions based on N-phosphonomethylglycine or its derivatives which are also able to contain adjuvants, such as inorganic ammonium salts, in concentrations clearly higher than those of similar compositions known in the prior art.

10 Another aim of the present invention is to provide concentrates based on N-phosphonomethylglycine or its derivatives which give rise to dilute spraying mixtures having a good herbicidal activity.

Another aim of the present invention is to provide  
15 concentrated compositions which are based on N-phosphonomethylglycine or its derivatives and also contain one or more surfactants having an activator action, that is to say having an action promoting the biological activity of the active substance, and in  
20 particular its herbicidal activity.

Another aim of the present invention is to provide concentrated compositions which are based on N-phosphonomethylglycine or its derivatives and have favourable properties, such as a good and rapid  
25 dispersibility in water.

Another aim of the present invention is to provide concentrated compositions which are based on N-phosphonomethylglycine or its derivatives and have

favourable properties, such as a good fluidity at low temperature.

Another aim of the present invention is to provide concentrated compositions which are based on N-phosphonomethylglycine or its derivatives and have  
5 favourable properties, such as a low tendency to produce foam, which enables lower quantities of anti-foam to be used.

Yet another aim of the present invention is to  
10 provide concentrated compositions, or formulations, (also termed concentrates) based on N-phosphonomethylglycine and especially simple N-phosphonomethylglycine which is sparingly soluble in water.

Another aim of the present invention is to provide  
15 compositions based on N-phosphonomethylglycine having the abovementioned advantages, these compositions also containing one or more other herbicides.

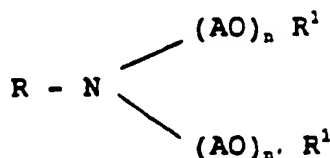
It has now been found that these aims can be achieved, in whole or in part, by virtue of the  
20 compositions according to the invention. Where there is no specific indication, the percentages in the text which follows are percentages in weight/volume.

Moreover, glyphosate equivalent is used to designate the corresponding amount of product as if all of the  
25 N-phosphonomethylglycine derivative were in the form of ordinary N-phosphonomethylglycine.

These compositions are liquid compositions consisting of (concentrated) suspensions in an organic,

or possibly aqueous-organic, solvent medium,  
containing:

- a) N-phosphonomethylglycine and/or one of its derivatives having an inherent solubility in water of more than 5 g/l, preferably more than 9 g/l, this N-phosphonomethylglycine and/or its derivative being present in the compositions in a proportion of at least 100 g/l glyphosate equivalent, at least part of this N-phosphonomethylglycine or its derivatives being in a form insoluble in the medium under consideration (the insolubility results in particular from the fact that the amount of N-phosphonomethylglycine and/or of its derivative exceeds the solubility limit in the medium),
- b) a surfactant having an activator character and having the formula



in which

- R is a straight-chain or branched alkyl or alkenyl hydrocarbon chain having from 8 to 22 carbon atoms,

A represents an alkylene group, preferably ethylene or propylene,

- n and n' are integers such that n + n' is between 2 and 40, preferably between 16 and 30 and still more preferentially between 20 and 25, and

R<sup>1</sup> is a hydrogen atom or an acyl radical such as formyl, acetyl, propionyl (that is to say CH<sub>3</sub>-CH<sub>2</sub>-CO) or

benzoyl.

Of course, it is possible to replace this single activator surfactant by a mixture of surfactants in which, on average, R, n and n' correspond to the definitions given above.

The herbicidal active substance used in the invention is thus N-phosphonomethylglycine and/or one of its derivatives having an inherent solubility in water of more than 5 g/l and preferably more than 9 g/l. Derivatives which may be used are the very numerous derivatives of N-phosphonomethylglycine known per se, in particular the salts, taken on their own or as mixtures. The following may be mentioned amongst the most appropriate derivatives: the sodium, potassium or inorganic or organic ammonium salts, in particular the isopropylammonium salts, and the sulphonium salts; N-methyl-N-(methylsulphonyl)-N',N'-(phosphonomethyl)-glycylamine; the aluminium salt is not included in the invention. Of course, the use of these products must respect the percentage and solubility conditions indicated elsewhere.

Advantageously, the present invention relates to concentrated compositions of the type described above and also having one and/or the other of the following characteristics:

a) the N-phosphonomethylglycine or its derivative is in an amount in excess of the solubility limit in the medium under consideration, preferably of between 120

and 250 g/l and still more preferentially between 160 and 220 g/l; the proportion of undissolved N-phosphonomethylglycine derivative is greater than 30 % and preferably greater than 75 %.

- 5 b) N-Phosphonomethylglycine, or its derivative, which is insoluble, is in the form of solid particles having a diameter of less than 30 microns and preferably of between 1 and 20 microns.

- c) The concentrated composition contains an ammonium  
10  $(\text{NH}_4^+)$  salt such as the nitrate, the phosphate, the sulphonate, the thiocyanate or preferably the sulphate, in a proportion of 100 to 500 g/l, preferably 200 to 350 g/l.

- d) The concentrated compositions are intended to be  
15 diluted by the agriculturalists in containers containing water so as to be able to spread these dilute spraying mixtures at a rate of 100 to 600 l/ha, the active material itself being applied at a rate of 0.125 to 1.5 kg/ha.

- 20 e) The weight ratio glyphosate equivalent  
surfactant (activator)

is between 0.5 and 6 and preferably between 0.6 and 2. This relatively large amount of surfactant relates to this surfactant having a biological activator/herbicide  
25 character, it being understood that the composition according to the invention can also contain, as will be specified below, all types of other components and in particular of surface-active agents (or surfactants) of



very diverse nature having a wetting or dispersing or emulsifying character; these surfactants are then used in dosages very much lower than the dosage of activator.

- 5 f) The solvent is an organic solvent, preferably miscible with water, which can contain up to 50 % of water, preferably less than 30 %, the said solvent being such that N-phosphonomethylglycine is sparingly soluble therein, that is to say soluble to the extent  
10 of less than 80 g/l and preferably of less than 40 g/l.

The concentrated suspensions according to the invention are prepared in a manner such as to obtain a stable fluid product which does not settle (fine grinding).

- 15 They usually contain from 10 to 75 % of active substances (herbicides), from 0.5 to 40 % of surfactant(s) having an activator character, from 10 to 50 % of an ammonium salt (adjuvant), from 0.1 to 10 % of ordinary surfactant(s), that is to say having a  
20 dispersing and/or wetting and/or emulsifying character, and from 0 to 30 % of appropriate additives, such as anti-foams, corrosion inhibitors, protective colloids, thickeners, sequestering agents, thixotropic or pseudoplastic agents, stabilizers, penetrating agents  
25 and adhesives, and, as carrier, an organic liquid in which the active substance is sparingly soluble or insoluble. Some organic solid substances or inorganic salts can be dissolved or in suspension in the carrier

to assist in preventing sedimentation, or as antigels. More generally, the compounds used in the invention can be combined with all solid or liquid additives corresponding to customary formulation techniques.

5        In addition to N-phosphonomethylglycine and/or its derivatives, the compositions used in the invention can contain other known active substances having herbicidal properties or plant growth-regulating properties.

10        The following may be mentioned as herbicidal substances which can be mixed with the glyphosate derivatives in the compositions according to the invention: acifluorfen, acetonifene, bifenox, diflufenican, asulam, the triazines (in particular simazine and atrazine), diuron and oxadiazon, 15 herbicides of the hormone or phenoxy types, in particular 2,4-D, 2,4-DB, MCPP, hydroxybenzotriazoles (in particular bromoxynil and ioxynil), imidazolinones (in particular imazaquin and imazapic), and sulphonylureas (in particular chlorsulphuron and 20 metsulphuron). The above names are standardized names for designation of herbicides.

      These herbicides are most frequently used in a proportion of from 1 to 400 parts by weight per 100 parts of glyphosate or glyphosate equivalent. By 25 using the term glyphosate equivalent, the calculation of the parts is thus reduced to as if all of the glyphosate derivatives were in the form of N-phosphonomethylglycine.

More precisely, when herbicidal active substances other than glyphosate are used and mixed with glyphosate, the following proportions are generally used for the weight ratio wr:

5	glyphosate or glyphosate equivalent (wr is equal to _____)	
	other herbicide	
	glyphosate + acifluorfen:	$\frac{4}{100} \leq wr \leq \frac{9}{100}$
10	glyphosate + diuron or oxadiazon:	$2 \leq wr \leq 4$
	glyphosate + aclonifen:	$\frac{1}{3} \leq wr \leq \frac{10}{3}$
	glyphosate + bifenox:	$\frac{1}{3} \leq wr \leq 1$
15	glyphosate + diflufenican:	$2 \leq wr \leq 20$
	glyphosate + asulam:	$\frac{1}{4} \leq wr \leq 1$
	glyphosate + phenoxy:	$\frac{2}{3} \leq wr \leq 4$
20	glyphosate + hydroxybenzonitrile:	$1 \leq wr \leq 10$
	glyphosate + triazine:	$\frac{1}{3} \leq wr \leq 1$
	glyphosate + imidazolinone:	$1 \leq wr \leq 4$
	glyphosate + sulphonylurea:	$\frac{100}{6} \leq wr \leq 100$
25		6

In accordance with what has already been stated, the concentrated suspensions according to the invention

contain an organic solvent (or some times termed carrier). This solvent is a natural or synthetic organic or inorganic substance with which the active substance or substances are combined to facilitate their application to the plant or to the soil. This solvent is therefore generally inert and acceptable in agriculture, in particular on the treated plant. In the present invention, the solvent can therefore be an organic liquid such as, for example, esters, in particular methyl glycol acetate; ketones, in particular cyclohexanone and isophorone, petroleum fractions; aromatic hydrocarbons, in particular the xylenes, or paraffin hydrocarbons; aliphatic or aromatic chlorinated hydrocarbons, in particular the chlorobenzenes, glycols, liquid oligoglycols or polyglycols, that is to say of low molecular weight, or vegetable oils, which may be esterified.

In accordance with what has already been stated, the concentrated compositions according to the invention can contain one or more surfactants in addition to the surfactant having an activator character defined further above. The surfactant used can be an emulsifying agent, dispersing agent or wetting agent of the ionic or nonionic type or a mixture of such surfactants. Examples which may be mentioned are salts of polyacrylic acids, salts of lignosulphonic acids, salts of phenylsulphonic or naphthalene sulphonic acids, polycondensation products

of ethylen oxid with fatty alcohols r fatty acids r fatty amines, substituted phenols (in particular alkylphenols or arylphenols), the salts of sulphosuccinic acid esters, taurine derivatives (in particular alkyltaurates), the phosphoric esters of alcohols or of polycondensation products of ethylene oxide with phenols, esters of fatty acids and polyols, and the derivatives of the above compounds containing sulphate, sulphonate and phosphate functions.

The following examples, given as non-limiting examples, illustrate the invention, in particular the concentrated suspensions according to the invention and their use, and show how this invention can be implemented.

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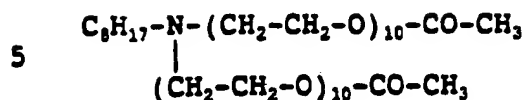
## EXAMPLE 1

	N-Phosphonomethylglycine (acid)	200 g/l
	Ammonium sulphate (adjuvant)	200 g/l
	Surfactant (activator) defined below:	200 g/l
	Dispersing agents/wetting agents:	
20	polycondensation products of ethylene oxide with tris(phenylethyl)phenol phosphate	20 g/l
	ammonium dodecylbenzenesulphonate	10 g/l
	Organopolysiloxane oil (anti-foam)	2 g/l
25	Bentonite (thixotropic agent)	2 g/l
	Polyvinyl alcohol (protective colloid)	8 g/l
	Solvents:	
	propylene glycol	300 g/l

water

250 g/l

The surfactant used in this example was a product of formula



This mixture is ground in a ball mill so as to obtain a concentrated microsuspension in which 73 % of the N-phosphonomethylglycine is in suspension in the form of particles having a size of between 5 and 20 microns. One fraction of this concentrated suspension is treated by centrifuging; after analysis of the liquid phase, 27 g/l of N-phosphonomethylglycine are found in this liquid phase.

15 This concentrated composition retains its physicochemical properties

- a) after standing for one month at 50°C, and also
- b) after standing for one month divided into eight periods of equal duration, four at 35°C and four at -10°C, alternately.

20 A concentrated composition such as prepared in the present example is then diluted in water using one litre of concentrate per 100 litres of water. A dilute and homogeneous spraying mixture is thus obtained, virtually instantaneously, which is sprayed at a rate of 250 l/ha on the following weeds: Portulaca oleraceae, Centaurea cyanus, Sinapis arvensis, Panicum trichoides and Abutilon theophrasti. Using a dosage of active substance of 500 g/ha, the above weeds are

destroyed at respective degrees of destruction of 95 %, 100 %, 98 %, 100 % and 100 %.

## EXAMPLE 2

	N-Phosphonomethylglycine (acid)	200 g/l
5	Ammonium sulphate (adjuvant)	200 g/l
	Surfactant (activator) used in Example 1:	200 g/l
	Dispersing agents/wetting agents:	
	polycondensation products of ethylene oxide with tris(phenylethyl)phenol phosphate	20 g/l
10	ammonium dodecylbenzenesulphonate	10 g/l
	Organopolysiloxane oil (anti-foam)	2 g/l
	Polyvinyl alcohol (protective colloid)	8 g/l
	Bentonite (thixotropic agent)	2 g/l
15	Solvent:	
	polyethylene glycol (molecular weight = 400)	552 g/l
	This mixture is ground as in Example 1 and has the same stability characteristics as the concentrated	
20	composition of Example 1.	

## EXAMPLE 3

	N-Phosphonomethylglycine (acid)	125 g/l
	Oxadiazon	125 g/l
	Surfactant used in Example 1:	125 g/l
25	$(\text{NH}_4)_2\text{SO}_4$	125 g/l
	Dispersing agents/wetting agents:	
	polycondensation products of ethylene oxide with tris(phenylethyl)phenol	

	phosphate	20 g/l
	ammonium dodecylbenzenesulphonate	10 g/l
	polycondensation products of ethylene oxide with dodecanol (20 EO)	50 g/l
5	Organopolysiloxane oil	2 g/l
	Bentonite (thixotropic agent)	2 g/l
	Polyvinyl alcohol (protective colloid)	8 g/l
	Solvent:	

	polyethylene glycol (MW = 400)	410 g/l
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- 10 This mixture is ground as in Example 1 and has the same stability characteristics as the concentrated composition of Example 1.

## EXAMPLE 4

	N-Phosphonomethylglycine (acid)	125 g/l
15	Acclonifen	250 g/l
	Surfactant used in Example 1:	125 g/l
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	125 g/l

Dispersing agents/wetting agents:

	polycondensation products of ethylene oxide with tris(phenylethyl)phenol	
20	phosphate	30 g/l
	Propylene glycol	270 g/l
	H <sub>2</sub> O	175 g/l

- 25 This mixture is ground as in Example 1 and has the same stability characteristics as the concentrated composition of Example 1.

## EXAMPLE 5

	N-Phosphonomethylglycin (acid)	200 g/l
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Chlorsulphuron	2 g/l
Surfactant used in Example 1:	200 g/l
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	200 g/l

Dispersing agents/wetting agents:

5	polycondensation products of ethylene oxide with tris(phenylethyl)phenol phosphate	14 g/l
	A 4:1 ethylene oxide/dodecanol condensation product	14 g/l
10	A 6:1 ethylene oxide/decanol condensation product	40 g/l
	Attapulgate (thixotropic agent)	8 g/l

Solvents in an amount sufficient for 1 l:

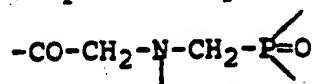
aromatic hydrocarbons, petroleum distillation fraction containing C<sub>6</sub> to C<sub>11</sub> compounds.

This mixture is ground as in Example 1 and has the same stability characteristics as the concentrated composition of Example 1.

This concentrated composition is diluted so as to spread 750 g/ha of active substance and 300 l/ha of dilute spraying mixture over land infested with weeds. The following degrees of destruction are observed on the treated weeds: 99.7 % (Centauria cyanus), 97.5 % (chrysanthemum), 80 % (Galium aparine), 85 % (Sinapis alba), 92.5 % (Sinapis arvensis), 92.5 % (Stellaria media), 93.5 % (Agrotis t. nuis), 96.5 % (Alopecurus myosuroides), 98.5 % (Avena fatua), 97.6 % (Lolium multiflorum), 97.6 % (Phalaris canariensis) and 82.5 %

(Poa annua).

By the term "N-phosphonomethylglycine derivative" it is meant a compound comprising the group



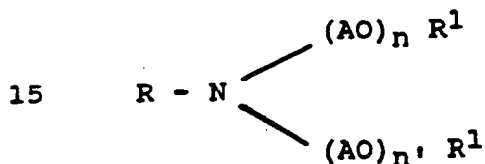
- 5 preferably a salt, ester or amide, for example of N-phosphonomethylglycine itself. Sulfonamides comprising a group of the formula defined above are also included.

CLAIMS

1. An organic or aqueous-organic composition comprising a suspension of N-phosphonomethylglycine and/or one of its derivatives, which comprises:

a) N-phosphonomethylglycine and/or one of its  
5 derivatives having an inherent solubility in water of more than 5 g/l, this N-phosphonomethylglycine and/or its derivative being present in the composition in a proportion of at least 100 g/l glyphosate equivalent, at least part of this N-phosphonomethylglycine or its derivatives being in a  
10 form insoluble in the organic or aqueous organic medium of the composition,

b) an activating surfactant having an activator character and having the formula



in which

R is a straight-chain or branched alkyl or alkenyl hydrocarbon chain having from 8 to 22 carbon atoms,

20      A represents an alkylene group,

n and n' are integers such that n + n' is from 2 to 40,

R<sup>1</sup> is a hydrogen atom or an acyl radical

2. A composition according to claim 1 in which  
25 the N-phosphonomethylglycine and/or one of its derivatives

has an inherent solubility in water of more than 9 g/l.

3. A composition according to claim 1 or 2 in which the alkylene group A is ethylene or propylene.

4. A composition according to any one of the  
5 preceding claims in which  $R^1$  is formyl, acetyl, propionyl or benzoyl.

5. A composition according to any one of the preceding claims wherein  $n + n'$  is from 16 to 30.

6. A composition according to claim 5 wherein  
10  $n + n'$  is from 20 to 25.

7. A composition according to any one of the preceding claims wherein the N-phosphonomethylglycine derivative is chosen from the group consisting of the sodium, potassium or inorganic or organic ammonium salts,  
15 and the sulphonium salts, taken individually or as a mixture.

8. A composition according to claim 7 in which the organic ammonium salt is the isopropylammonium salt.

9. A composition according to any one of the  
20 preceding claims wherein N-phosphonomethylglycine or its derivative is present in an amount in excess of the solubility limit in the medium under consideration.

10. A composition according to claim 9 wherein the N-phosphonomethylglycine or its derivative is present in an  
25 amount of from 120 to 250 g/l.

11. A composition according to claim 10, wherein N-phosphonomethylglycine or its derivative is present in an amount of from 190 to 220 g/l.

12. A composition according to any one of the  
5 preceding claims wherein the proportion of undissolved N-phosphonomethylglycine derivative is greater than 30%.

13. A composition according to claim 12 wherein the proportion of undissolved N-phosphonomethylglycine derivative is greater than 75%.

10 14. A composition according to any one of the preceding claims, wherein N-phosphonomethylglycine, or its derivative, which is insoluble, is in the form of solid particles having a diameter of less than 30 microns.

15 15. A composition according to claim 14 wherein the solid particles have a diameter of between 1 and 20 microns.

16. A composition according to any one of the preceding claims, which contains an adjuvant such as an ammonium salt, this salt being a nitrate or a phosphate or  
20 a sulphamate or a thiocyanate or a sulphate.

17. A composition according to claim 16 which contains an adjuvant in a proportion of from 50 to 500 g/l.

18. A composition according to claim 17 which contains an adjuvant in a proportion of from 100 to 350  
25 g/l.

19. A composition according to any one of the preceding claims, suitable for dilution with water for application at a rate of 100 to 600 l/ha, the active substance itself being applied at a rate of 0.125 to 1.5 kg/ha.

20. A composition according to claim 1 substantially as hereinbefore described in any one of the Examples 1 to 5.